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*P. J. H. Boswell  
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RETARDED DIFFUSION AND RHYTHMIC PRECIPITATION.

BY

JOHN STANSFIELD.

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ART. I.—*Retarded Diffusion and Rhythmic Precipitation*;  
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*Historical.*

OWING to the fact that the greater part of the literature of this subject is in the German language, it has been considered advisable to give the following somewhat detailed account of it.

The rhythmic precipitates formed by diffusion of reagents in gelatine or other media, now generally known as Liesegang rings, were first described in a publication which is not generally available \* (1). The precipitates appear to have been shown to W. Ostwald by Liesegang, as a result of which Ostwald published a short note regarding them (2). The ring-formed precipitates were formed by diffusion of silver nitrate from a drop placed upon a gelatine containing potassium chromate. Ostwald considered that the diffusion outward of the silver nitrate and the inward diffusion of the chromate resulted in the formation of silver chromate, which was present, at first, as a super-saturated solution in the meta-stable state. Consequent upon the solution of the labile state a precipitate formed removing the silver chromate in excess of saturation and the diffusion continued with similar results. As the removal of silver chromate continued the solutions became continuously more dilute, so that the precipitates were formed at continuously greater distances apart.

In 1903 Morse and Pierce (3) regarded the precipitation as certainly due to a super-saturation effect. They produced by diffusion ring precipitates of mercurous chromate, lead chromate, and Berlin blue, which had been obtained previously by Liesegang, and also ring precipitates of lead sulphate, silver

\* See literature references at the end of this paper.

carbonate, silver pyro-phosphate, silver thiocyanate, silver bromide, cobalt hydroxide, barium chromate, mercurous bromide, and carbon di-oxide, the last-named as rings of bubbles.

They performed experiments of a quantitative character, using capillary tubes containing a weak potassium chromate solution in gelatine, which were dipped into silver nitrate solutions of different strengths. The precipitates appeared suddenly as bands across the capillary tubes, and were observed and measured by means of a cathetometer, the times being observed at the formation of the precipitates. Assuming that the chromate solution is completely dissociated, they proved mathematically that the  $\frac{\text{distance}}{\sqrt{\text{time}}}$  for all the layers in all tubes with the same initial concentrations is constant. They gave twenty-three tables of observed figures, which show this constancy, within the limits of experimental error. At a lower temperature, with the same initial concentrations, the distances appear to be greater, i. e. the diffusion is more rapid at higher temperatures.

In a saturated solution, for equilibrium  $\text{Ag}_2' \times \text{CrO}_4'' = k$ . In an unsaturated solution, *fc.* equilibrium  $\text{Ag}_2' \times \text{CrO}_4'' = k$ .  $\text{AgCrO}_4$ . Is there a boundary which cannot be overstepped in a super-saturated solution without precipitation following? *e. g.* :—



Morse and Pierce found that for a given concentration of one ion a certain definite concentration of the other causes precipitation. They calculated that when precipitation takes place the concentrations of the solutions are  $\frac{N}{75}$  for the chromate and  $\frac{N}{200}$  for the silver. Both solutions must be fully dissociated at these dilutions. They calculated, further, that  $H$  is a definite super-saturation limit, which is  $1.4 \times 10^{-6}$  gram molecules per liter, at  $16^\circ \text{C}$ . They found that the diffusion is quicker in gelatine than in water, the diffusion constant calculated for silver nitrate being 1.24 cms. per day, that observed being 1.54. (They also suggested that the precipitate is colloidal, but this appears not to be the case.)

Small finer white lines are mentioned as forming between the main precipitates, which become red and then are obliterated when the main precipitate forms over them. These are said to be due to impurities, and are not formed in pure gelatine. They found that gelatine is not essential to the formation of the banded precipitates, *but that capillary tubes containing aqueous solutions give similar results*, and that the precipitates

break up, say after about four in series have been formed. When the experiment is performed in gelatine they are held in place and do not break up.

In 1904 Hausmann (4) carried out experiments with capillary tubes containing gelatine solutions of silver nitrate dipping into solutions of sodium chloride, etc., and found that the heights to which the precipitates extend in any given time depend on the concentration of the silver nitrate and of the sodium chloride, etc., also. Liesegang had claimed that equivalent weights of sodium chloride, strontium chloride, potassium bromide, and potassium iodide diffuse to equal heights in equal times. Hausmann found that the distances varied with the reagents, with their concentrations, and with the concentrations of the gelatine. In some of the reactions banded precipitates were formed.

Mention is made of little brown bands between the main ones and also to secondary rings in the upper part of the tube, which are broader than those in the lower part and increase in breadth upwards. With increase of gelatine concentration the bands were found to be brought closer together. (Curves given pp. 117, 118, loc. cit.)

The precipitation of metallic sulphides is discussed. Certain compounds are formed in the colloidal state, e. g., silver iodide, mercuric oxide, ferric hydroxide, copper hydroxide, and copper ferro-cyanide. The following substances were formed in non-banded crystalline precipitates:—barium sulphate, strontium sulphate, calcium sulphate, barium oxalate, silver oxalate, thallium chloride, bromide and iodide. In certain reactions compounds separate out which are not stable at atmospheric temperatures under normal conditions, e. g. the yellow form of mercuric iodide, which is stable above 126° C., and certain thallium salts.

Attention is called to the results obtained by Larsen on cooling a salt solution whose concentration decreases at higher temperatures. Regular layers are formed with increasing distances between them, and having decreasing concentrations, upward (5).

With regard to the banded precipitates Hausmann suggests that the compounds are present in the colloidal state before precipitation which only ensues upon super-saturation.

By diffusing different chlorides against a constant strength of silver nitrate he showed that the distances diffused were independent of the metal combined with the chlorine, depending only on the silver and chlor-ion, their speeds of diffusion and concentrations. As the concentration of the chloride decreases it is able to penetrate less and less into the (slightly less than  $\frac{N}{400}$ ) silver nitrate. Weaker solutions of copper and

iron chlorides penetrate farther, perhaps because hydroxyl ions are present. Cadmium chloride diffuses more slowly in a stronger solution, possibly due to association.

By diffusing different salts of silver into gelatines containing the same reacting salts, in the same concentrations, the reactions were found to proceed at the same speed regardless of the combined ion, showing that the silver ion is the important one for the reaction.

Solutions of potassium chloride, bromide and iodide were diffused against silver nitrate, the distances being measured, with the following results:

|                             |      |                         |    |        |
|-----------------------------|------|-------------------------|----|--------|
| Ratio of distances diffused | AgBr | 1.034 Vel. of diffusion | Br | 1.0366 |
|                             | AgCl |                         | Cl |        |
|                             | AgBr | 1.017                   | Br | 1.0185 |
|                             | AgI  |                         | I  |        |
|                             | AgI  | 1.0167                  | I  | 1.0146 |
|                             | AgCl |                         | Cl |        |

Other cases gave equally satisfactory results, while some gave discordant results.

Hausmann thus proved that the reaction depends only on the ions involved in the precipitate, and not on those combined with them, and that the speed of the reaction depends on the ion which diffuses into the jelly and not on the one which is present in the jelly. He also confirmed the result of Morse

and Pierce (see page 1) that  $\frac{\text{distance}}{\sqrt{\text{time}}}$  is constant. He pointed out that this constitutes the first non-electric method of determining diffusion velocities.

In 1905 Bechhold (6) called attention to the importance of rhythmic precipitation in the development of layers of silica, horn, and calcium carbonate in sponges, the development of layered calcareous shells in the perforated Foraminifera, in gasteropod and lamellibranch shells, the development of layers in the bones of some vertebrates, and its importance in intussusception in plants.

Bechhold agrees with Ostwald concerning the super-saturation idea. He used ammonium chromate or bichromate in making ring precipitates and found that owing to the fact that silver chromate is slightly soluble in ammonium salts that the bands are more widely spaced. He mentioned the strong contractive forces which are set up in gelatine when silver nitrate is added to it, and suggested that these forces may have something to do with the formation of the rings. But this appears not to be the case because under crossed nicols there is not a maximum brightness between the bands.



He found that on diffusing ammonium chromate into a silver solution in gelatine no precipitate forms. In the diffusion of silver nitrate by increasing the ammonium nitrate thicker rings were obtained.

In 1907 Liesegang (7) showed that a later set of rings may be formed cutting across an earlier set, apparently without being disturbed or influenced by the rings already present. Close examination shows that the earlier formed rings are extended in comb-like forms to a very small distance by the second deposition. But the "sowing" action of the first formed precipitates is almost negligible.

In 1912 Hatschek (8) produced by diffusion in gelatine, agar-agar or in silicic acid precipitates of calcium sulphate, and carbonate, barium carbonate, sulphate and chromate, lead chloride, iodide, bromide, chromate, ferro-cyanide, ferri-cyanide, strontium carbonate, sulphate, phosphate, oxalate and silicofluoride, copper phosphate, cadmium sulphide, manganese ferro-cyanide, silver bichromate, and silicofluorides of sodium and potassium. Some of these were always formed in layers and some always as macroscopic crystals. According to Hatschek the results are always the same, no matter which ion diffuses into the jelly containing the other ion.

With a view to testing the super-saturation theory of Ostwald he impregnated a jelly with lead iodide and potassium iodide, diffusing a solution of lead into it. The rings of lead iodide were formed just as though the medium were not sown with lead iodide. He holds that super-saturation cannot be used as a general explanation of the formation of precipitates in layers. The work of Liesegang quoted above would appear to invalidate this conclusion.

In 1914 Liesegang (9) claimed that the presence of a small amount of acid and of gelatose is necessary for the formation of the rings in gelatine, none being formed in pure gelatine. If the amount of acid is increased the rings do not appear, so that a definite amount is essential. By increasing the amount of acid present the silver chromate, which is soluble in acid, is enabled to diffuse to a greater distance before precipitation takes place. The result is the bands are more widely spaced, and are thicker. Finally, by greater increase of the acid the silver chromate forms as a continuous mass. Spiral bands were produced, and an examination of some of the older published figures reveals the fact that they are spiral and not actually rings as they were thought to be. Liesegang mentions the presence of spirals on the retina in some birds.

When the drops of silver nitrate from which the diffusion proceeds are not circular, cracks appear, cutting the bands, and are free from precipitate. This shows how short spaces may

separate the ends of bands without the formation of precipitate by "sowing." The formation of the rings is due to the production of super-saturation at innumerable individual points. Thus the spiral form does not afford any difficulty to the super-saturation hypothesis.

Bradford (10) has recently investigated the effect of the by-products of the reactions resulting in the formation of the ring precipitates, and by varying the concentration of the by-product was unable to affect their formation in any way. Hatschek had shown that the particles formed in the ring precipitates are larger than those obtainable in aqueous solutions. Bradford suggests that this phenomenon is due to adsorption by the precipitate of substance dissolved in the gel, which merely serves to retain the precipitate in place.

Bradford finds that the distances between the layers formed are roughly inversely proportional to the molar strength of the reagent in the gel, and not to that of the diffusing reagent.

In a more recent paper (11) the same author has developed the idea of adsorption in connection with the formation of banded precipitates. It might be suggested that the term pseudo-stratification would be preferable to stratification as used by him.

#### *Retarded Diffusion and Rhythmic Precipitation.*

By reason of its application to geology the subject of rhythmic precipitation has assumed an importance to geologists which cannot be neglected. In connection with an investigation of Eozoon the writer had occasion to consider the question of the causes governing the formation of rhythmic precipitates. A series of experiments has been made in order to afford a basis for a comparison with banded structures in rocks. The experiments were carried out using diffusion from a drop placed upon a gelatine layer on a glass plate, as described by Liesegang. The gelatine was prepared according to his directions by preparatory washing in several portions of distilled water, to remove some but not all of the impurities, then dissolving in distilled water, a convenient concentration for use at a room temperature of  $12^{\circ}$  C. being 1 gr. of gelatine in 35 c.c. water. The solution was used after standing one or two days, reheating the jellied mass to bring it to the liquid state again, care being taken both in the solution and re-solution of the gelatine to avoid over-heating. Care was taken to keep the relative gelatine concentrations the same in any set of experiments. This was done by adding 1 c.c. of a solution ten times as strong as the one to be investigated to 9 c.c. of the gelatine solution. Thus a gelatine solution of known strength was obtained, containing any desired concentration of the reagent to be exam-



ined. This was poured out on to several glass plates and allowed to set, after which drops of the second reagent, of different strengths, were placed upon them. These solutions gradually diffused through the gelatine and precipitates were formed, sometimes continuously, sometimes in separated bands. (See figs. 1, 2, and 3.)

It is found that with different concentrations of the diffusing reagent (the one in the drop) against a constant concentration of the reagent in the gelatine the diffusion goes at different rates, the stronger solutions diffusing more quickly and to greater distances than the weaker. Again, by keeping the diffusing reagent constant and varying the concentration of the opposing reagent the diffusion is retarded by increasing the opposing concentration, and also the total distance of diffusion is decreased. When the molecular concentrations of the solutions approach closely there is a definite limit to the distance to which the stronger solution is able to diffuse. In many of the experiments the gelatine dried before the limit was reached, if any exists, with the solutions of more unequal concentrations, but with the solutions mentioned above the limit was clear, and was reached, in many cases, within a few hours.

The following tables for different experiments, showing the distances to which diffusion has taken place with different strengths of the reacting solutions, illustrates the point. The figures enclosed in a double line are for experiments using one batch of gelatine and are comparable with each other, but not strictly comparable with those within another double line, by reason of possible differences in the preparation of the gelatine.

The experiments which yielded clearly separated bands of precipitate are indicated by a small ring within the squares belonging to them. It is seen that the production of the bands in gelatine takes place best when a strong silver solution diffuses against a weak chromate solution. In those cases which did not show clearly separated bands, the precipitate appeared to be continuous, but examination with the hand lens or sometimes with the microscope showed that the bands were present, but that they were more closely spaced, so as to appear continuous. Some cases are clearly banded, to the naked eye, but with the stronger solutions this fine banding of the apparently uniform silver chromate can only be seen under the microscope.

When clearly separated bands are formed, our experiments have sometimes shown these passing into fragmentary banded layers toward the outside. In some cases this may be quite extensive, corresponding to ten or more bands. In other cases,

AgNO<sub>3</sub>

| 8N     | 6N   | 4N     | 2N   | N     | N/2    | N/4  | N/6  | N/10 |       |                                 |
|--------|------|--------|------|-------|--------|------|------|------|-------|---------------------------------|
| ·235   | 145  | ·09    | ·08  | —     |        |      |      |      | N/2   |                                 |
| ·45    | ·3   | ·25    | ·14  | —     |        |      |      |      | N/4   |                                 |
| ·66    | ·59  | ·425   | ·28  | ·2    |        |      |      |      | N/6   |                                 |
| ·775   | ·705 | ·65    | ·435 | ·255  |        |      |      |      | N/10  |                                 |
| 1·11   | ·865 | (·875) | ·725 | ·55   | ·2     | ·1   | —    | —    | N/20  |                                 |
| 1·275  | 1·12 | 1·03   | ·85  | ·77   | ·365   | ·16  | ·1   | —    | N/40  |                                 |
| 1·4    | 1·28 | 1·2    | 1·1  | ·775  | ·5     | ·18  | ·11  | —    | N/60  | K <sub>2</sub> CrO <sub>4</sub> |
| 1·46   | 1·31 | 1·26   | 1·11 | 1·1   | ·62    | ·375 | ·26  | ·24  | N/80  |                                 |
| (1·35) | 1·32 | (1·21) | 1·21 |       | ·65    | ·54  | ·31  | ·25  | N/100 |                                 |
| 1·54   | 1·47 | 1·4    | 1·28 | 1·27  | ·84    | ·6   | ·535 | ·41  | N/200 |                                 |
| ·115   | ·1   | ·085   | ·075 | —     |        |      |      |      | N/2   |                                 |
| ·285   | ·25  | ·24    | ·115 | —     |        |      |      |      | N/4   |                                 |
| ·375   | ·365 | ·325   | ·21  | ·1    |        |      |      |      | N/6   |                                 |
| ·47    | ·425 | ·4     | ·3   | ·19   |        |      |      |      | N/10  |                                 |
| ·625   | ·5   | (·525) | ·45  | ·335  | ·18    | ·1   | —    | —    | N/20  |                                 |
| ·725   | ·625 | ·6     | ·5   | ·425  | ·295   | ·16  | ·1   | —    | N/40  |                                 |
| ·79    | ·71  | ·71    | ·635 | ·51   | ·345   | ·175 | ·11  | —    | N/60  | K <sub>2</sub> CrO <sub>4</sub> |
| ·83    | ·75  | ·73    | ·675 | (·76) | (·445) | ·305 | ·225 | ·21  | N/80  |                                 |
| (·79)  | ·76  | (·71)  | ·715 |       | ·435   | ·385 | ·225 | ·19  | N/100 |                                 |
| ·85    | ·84  | ·8     | ·75  | ·74   | ·54    | ·425 | ·35  | ·28  | N/200 |                                 |

this is followed, on the outside, by an area in which the precipitate occurs as a continuous non-banded area containing the precipitate as small granules.

In other cases the fragmentation is not so prominent and the non-banded area of "disseminated" precipitate is followed outward by "secondary" bands of precipitate, which differ from the "primary" ones within, in that they are evenly spaced and not farther apart, with greater distance from the center, and in being made up of large, irregularly shaped grains of silver chromate, sometimes separate from each other, whereas the "primary" bands are continuous and consist of exceedingly minute granules of silver chromate. (See fig. 1.) There is always a clear "halo" outside the circle of diffusion which appears to be free from precipitate, but under the microscope is seen to contain minute grains of silver chromate. In some cases "subsidiary" bands have been noticed in this "halo." They correspond to the very fine lines noticed by the earlier workers and ascribed, by them, to the presence of impurities in the gelatine.

$K_2CrO_4$

A set of experiments was made with silver nitrate in the gelatine and potassium chromate as the "dominant" reagent in the central drop, having the higher molecular concentration. The results in this case were remarkably interesting. The following table gives the scheme of concentrations used. Numbers 26 to 30 showed only isolated spots or granules formed here and there in the gelatine as the chromate diffused outward. Numbers 21 to 25 showed the beginning of a very indefinite arrangement of the spots in bands. Numbers 16 to 20 showed an inner set of apparently continuous bands consisting of large granules of silver chromate followed by a space with the precipitate as isolated granules, and outside this again the arrangement in bands as in 21 to 25, but more clearly shown. (See fig. 4.) The inner bands are less well shown the stronger the chromate solution. The outer bands often show discontinuity and

Table (p. 8) showing distances diffused in a radial direction, measured in centimeters. The head of the column shows the strength of the silver nitrate solution diffusing and the strength of the potassium chromate solution in the gelatine is indicated at the extreme right. Upper left part of table—distances diffused after 6 hrs. 15 mins. Upper right, after 6 hrs. Lower left, after 1 hr. 50 mins. Lower right, after 2 hrs.

The results which show discrepancies are indicated by parentheses. These are due to inaccuracies in measurement. Those which recur in the same positions in both parts of the table are due to incorrect measurement of the size of the original drop, the others to inaccuracies in those individual measurements. The figures on the right side of the table are comparable with each other, and those on the left side with each other, but as they were obtained from experiments using two separately prepared batches of gelatine, the figures on the left are not comparable with those on the right, except in a general way.

$K_2CrO_4$

relative displacement of the bands, which are doubtless due to inequalities of diffusion. Both the inner and outer bands are more widely spaced toward the outside.

Numbers 12 to 15 show similar bands to those in 16 to 20. Numbers 1 to 11 show three similar areas, but in 1 to 7 there appears to be a continuous precipitate round the drop. This

| $K_2CrO_4$ |       |    |     |      |      |
|------------|-------|----|-----|------|------|
|            | 3N    | N  | N/2 | N/10 | N/20 |
| N/10       | 1     | 2  | 3   |      |      |
| N/20       | 4     | 5  | 6   | 7    |      |
| N/40       | 8     | 9  | 10  | 11   |      |
| AgNO       | N/80  | 12 | 13  | 14   | 15   |
|            | N/100 | 16 | 17  | 18   | 19   |
|            | N/200 | 21 | 22  | 23   | 24   |
|            | N/400 | 26 | 27  | 28   | 29   |
|            |       |    |     | 30   |      |

The strength of the potassium chromate in the drop in any experiment is given by the heading of the column in which the number falls, the strength of the silver nitrate in the gelatine being given at the extreme left, thus in the case of number 13 normal potassium chromate diffused into a gelatine containing an eightieth normal solution of silver nitrate.

is seen to have bands on the surface as with the stronger silver solutions cited above.

The experiments with the weakest silver solutions ( $\frac{N}{100}$ ) show that bands are not produced unless a certain concentration is present. From this it may be argued that the areas between the two sets of bands, in numbers 1 to 20, had an insufficient concentration of silver ions to allow of the formation of bands, as a result of the removal of silver ions by precipitation, the precipitation being followed by decrease of concentration outside the bands as a result of diffusion of silver ions inward to take the

place of those precipitated. The result is somewhat analogous to the thinning of a sheet of rubber by stretching. With the diffusion of the chroma-tions farther outward, however, a sufficient concentration of silver ions to allow of the formation of bands will again be met with and the "secondary" bands will result.

A similar explanation would apply to the unbanded layer in results cited above with diffusion of silver against a weaker solution of chromate. (See figs. 1 and 2.) It is possible, how-

FIG. 1.



FIG. 1.  $\times 3$ . The result of diffusion of 6N silver nitrate into a gelatine containing N 200 potassium chromate. The drop is surrounded by an area of apparently continuous precipitate, which actually shows fine bands on its surface. This passes outwards into the zone in which the bands are clearly separated, and become more widely spaced. Outside this zone is a non-banded zone of granular precipitate, beyond this a zone of granular precipitate arranged in evenly spaced bands. This is followed by a clear "halo." It is probable that the potassium chromate may not have been thoroughly mixed with the gelatine so as to give uniform conditions. At one point the non-banded zone is crossed by a narrow strip of bands. This is doubtless due to the presence of a streak of gelatine richer in potassium chromate than the rest. The unequal extensions in a radial direction of the inner banded zone may be explained in a similar manner.

ever, that this explanation is too simple, and that the hydrions present may have to be taken into account.

Another question should be discussed at this point. In all the bands and in the non-banded layer in the experiments with diffusion outward of chromate, and in the outer bands and the granular non-banded area in the case of outward diffusion of

FIG. 2.



FIG. 2.  $\times 5$ . A portion of the same (fig. 1) enlarged to show the character of the precipitate in the "granular" zones.

silver, the precipitate consists of large isolated granules sometimes taking on irregular shapes, in the more pronounced and well-marked bands, probably as a result of accretion of several granules. (See figs. 1 and 2.) But in the "primary" bands of the outward silver diffusion the precipitate is made up of exceedingly numerous and very small granules. In watching



the development of one of these bands under the microscope it was seen that the very numerous small granules were developed apparently independently of each other. The band grew quite slowly, being extended laterally. As it developed the central part extended itself in advance of the two sides, and

FIG. 3.



FIG. 3.  $\times 5$ . The result of the diffusion of 8N silver nitrate into a gelatine containing N. 60 potassium chromate. It shows the close bands (apparently a continuous mass of precipitate) passing outward into separated bands, which are broken toward the outside, and surrounded by a zone of "granular" precipitate and then by a clear "halo." The bands are broken by several clear channels. The bands on opposite sides of these are not directly opposite to each other, and they bend inwards toward the drop from which the diffusion took place. These may be explained by uneven distributions of concentrations of chromate or silver ions, or of both.

these followed, sometimes more slowly, sometimes more rapidly on the central part. Again, a little distance away from the

small cloud of granules, but along the line of the band, another cloud may appear, more thickly crowded with granules in the central line of the band. This would develop as before, in both directions, finally uniting with the other advancing part. The precipitate on each side of the central part gradually thickened. Thus, while the result is a series of bands of pre-

FIG. 4.

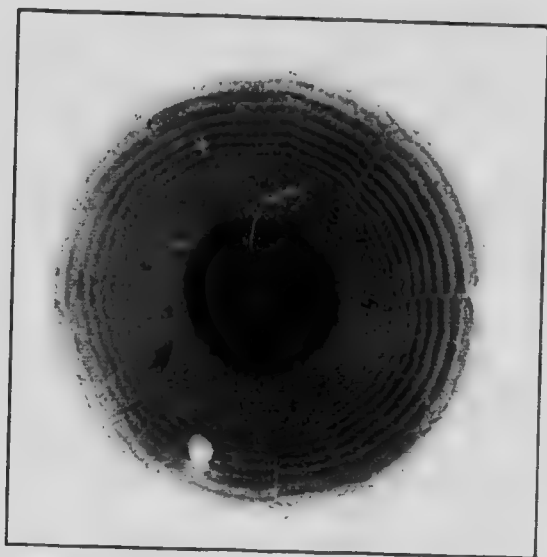
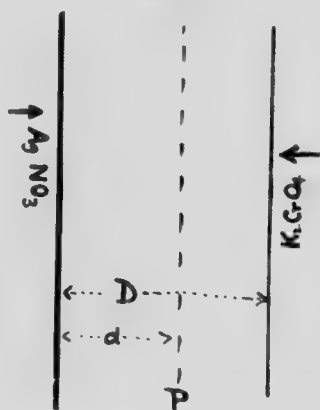


FIG. 4.  $\times 21.4$ . The result of the diffusion of N 10 potassium chromate into a gelatine containing N 100 silver nitrate. (No. 19.) There is an inner set of close bands round the drop, which appear to be continuous precipitate, in the photograph; outside this zone is one in which the precipitate occurs as isolated granules, and this is followed by bands in which the precipitate consists of separate large granules. Examination with a lens will show this. The outer bands are broken by clear channels, the bands being offset with regard to each other on opposite sides of the channels, in some cases. Both the inner and outer sets of bands become more widely spaced outwards.

precipitate, of apparently striking regularity, yet each separate small portion is developed independently of the rest at such point as the super-saturation boundary is over-stepped. We are able to understand more clearly, now, how the development of spiral forms may ensue, and how breaks may occur in the bands, with accompanying displacement of the bands (see fig. 4), and also the presence of cracks passing through the bands, which are free from precipitate, and along both sides of

which there may be a bending of the bands. (See fig. 3.) These are doubtless due to irregularities of the diffusion, and perhaps, in part, to irregular distribution of certain impurities or disturbing factors. The quite leisurely deposition of the very fine silver chromate granules suggests that each one is formed almost independently and kept independent, at least for some time, by the gelatine. The experiments of Hatschek and Liesegang investigating the possible sowing action of precipitate already in the gelatine have shown how little this action needs to be taken into account in the formation of the Liesegang rings. The question as to whether this isolation of precipitated granules is entirely due to the action of the gelatine

FIG. 3.



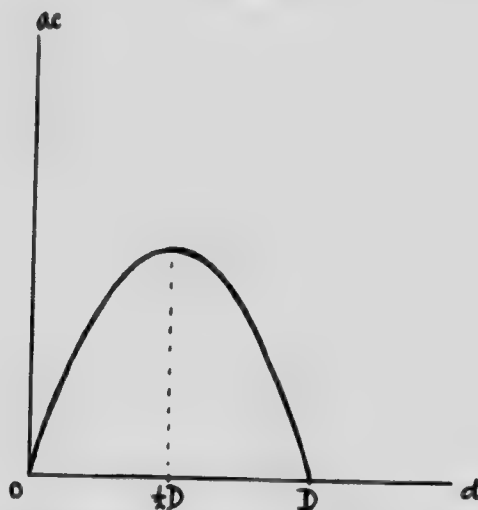
next arises. An experiment was made with diffusion of silver into a chromate-bearing gelatine to which a small amount of citric acid had been added. No banded precipitate was formed but a continuous precipitate in the colloidal state. That is to say, by increasing the concentration of hydrions the number of points at which precipitation takes place had been increased and the size of the particles resulting from precipitation had been decreased. (The definition of a colloid suspension being that the particles range in size somewhere between the limits of  $0.1\mu$  and  $1\mu\mu$  in diameter.)

In the case where the chromate solution is diffusing outwards this action of the hydrions appears to be prevented or very much curtailed, possibly owing to the potassions present. Also in the "secondary" bands of the silver diffusion this action appears to have been prevented. This is also probably due to the "dominance" of potassions relatively to the hydrions in

that part of the gelatine. Liesegang (9) has shown how gradual increase of hydrions present in a silver diffusion against chromate, in gelatine, results in the formation of broader bands, i. e., not only increases the number of centers of formation of the precipitate, but also increases the area over which these may form.

In a case where diffusion of silver from a drop and of chromate from a line drawn around the drop took place through a space free from both reagents, the first precipitate did not form at the point where the solutions first met. The silver diffusion

FIG. 6.



is quite visible as there is a clearly marked line in the gelatine at the outward front of the advancing solution. The first formed precipitate was situated about one millimeter within this line, i. e., nearer the center of the silver drop. This would suggest that the halo which surrounds the silver diffusion is an area in which the concentration is below the super-saturation boundary.

#### *Rate of Diffusion a Controlling Factor.*

From the foregoing it is seen that the explanation offered by Ostwald (see page 1) has been confirmed by later work. By the diffusion outwards of the silver and inwards of the chromate a depletion of the reservoirs of those ions takes place, i. e., the ionic concentration is gradually reduced, with the result that the silver ions are enabled to diffuse to a greater distance before the precipitation concentration is attained.

Thus ionic concentration is an important governing factor in determining the distances between the bands of precipitate.

Rate of diffusion is also an important factor, which has not been given adequate consideration in the past. Considering the case of silver chromate deposition, the rate of diffusion of the silver solution is greater than that of the chromate solution. So that, after the formation of one band the silver ions pass through it and outward beyond it, or continue onward from

FIG. 7.

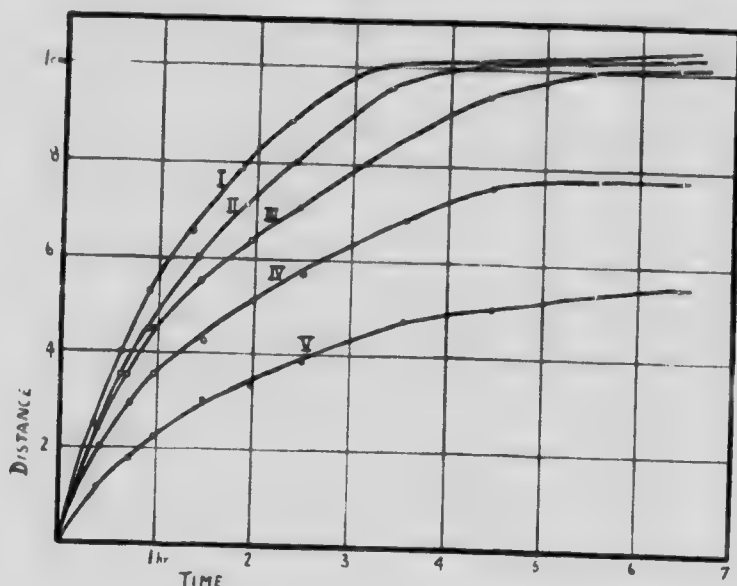


FIG. 7. Diffusion of silver nitrate against potassium chromate.

|      |    |                   |    |                                   |
|------|----|-------------------|----|-----------------------------------|
| I.   | 8N | AgNO <sub>3</sub> | N  | K <sub>2</sub> CrO <sub>4</sub> . |
| II.  | 4N | AgNO <sub>3</sub> | do |                                   |
| III. | 2N | do                | do |                                   |
| IV.  | N  | do                | do |                                   |
| V.   | N  | do                | N  | K <sub>2</sub> CrO <sub>4</sub> . |
|      |    |                   | 20 |                                   |

their position in front of it, before meeting the chromat-ions which have not yet crossed the free space. At such point as the concentration is high enough to give labile conditions precipitation ensues. The distance of this point from the last formed band must therefore depend upon the relative rates of diffusion of the two solutions. Thus, if other disturbing con-

ditions, such as gelatine concentration and amount of acid or other solute present, remain constant the distance between the rings depends upon the ionic concentrations and also upon the relative rates of diffusion. It thus appears that if in any reaction the increase in distance between the bands due to the effect of the difference of rates of diffusion could be counter-balanced by an equal effect in the opposite direction due to concentrations, the spaces between the bands would remain constant.

FIG. 8.

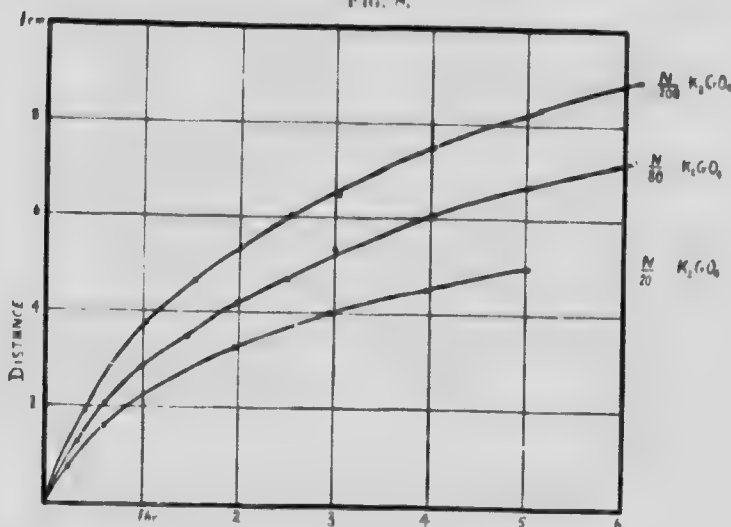


FIG. 8. Diffusion of normal lead nitrate against potassium chromate of different strengths.

Agate structure has been ascribed to the formation of Liesegang rings by diffusion of solutions through gelatinous silica. The discovery of gelatinous silica in a cavity in the Simplon tunnel is of interest in this connection. On examining certain agates the writer was struck by the fact that many of them show bands *which are equally spaced* and not at successively increasing distances, as in the ordinary Liesegang rings.

The writer does not consider that agates in general can be held to be produced by the Liesegang reaction; out of a large number examined but very few seem to be explicable only along these lines, by far the greater number allowing of other explanations. Each specimen of agate needs to be examined by itself, the history of each one being, of necessity, a separate entity, and only comparable with others by an accidental reproduction of a similar series of events.

Considering the formation of bands of silver chromate in outward diffusion of silver, if the concentrations for precipitation are  $A_0$  for the silver ions and  $C_0$  for the chromate ions and  $X_0$  for the silver chromate, then for equilibrium

$$A_0 C_0 = k X_0 \quad (1)$$

$k$  will vary with temperature.

Consider a space into which diffusion is taking place, just in front of a band of precipitate which is newly formed. The

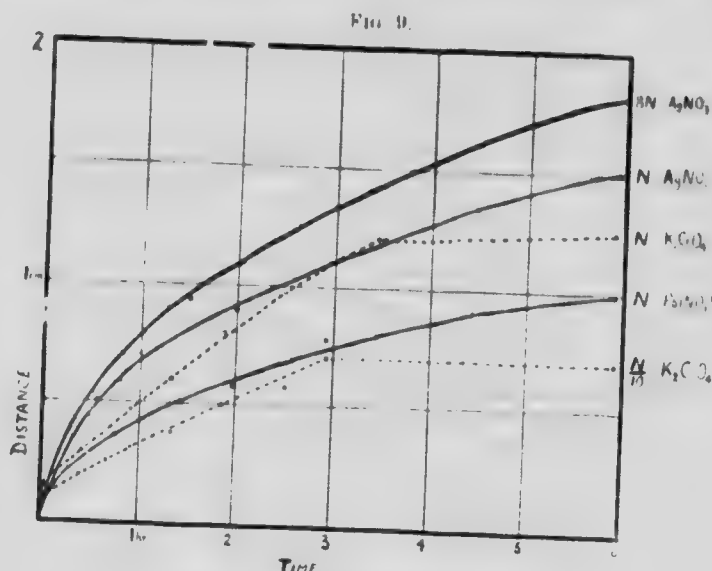


FIG. 9. Simple diffusion (no reaction).

silver ions are "dominant" and the chromate ions in excess of saturation of silver chromate have been removed from a certain space on each side of the band. The silver ions being "dominant" the value  $A_0$  is large compared with  $C_0$ , so that the silver ions may be regarded as starting their diffusion from the precipitate band (or, perhaps some plane outside it), while the chromate ions begin their diffusion from some plane at a distance  $D$  outside the band. (See fig. 5.) It should be noted that in keeping with the generally accepted conception regarding aqueous solutions the reagents involved will diffuse partly as molecules and partly as ions. When silver ions are referred to it is understood that each of these is associated with an oppositely charged nitrate ion the two charges neutralizing each other. For the purposes of discussion of the reaction with the



potassium chromate it is convenient to speak of the silver ions and chromate-ions, but the fact should not be lost sight of that these ions do not diffuse as isolated entities, but each charged ion must be associated with a charge of equal amount and opposite sign borne by some other ion or ions.

Suppose that the concentrations of the silver and chromate ions at the planes from which they begin to diffuse are  $a$  and  $c$  respectively, that the rates of diffusion are  $V_a$  and  $V_c$ , and that

FIG. 10.

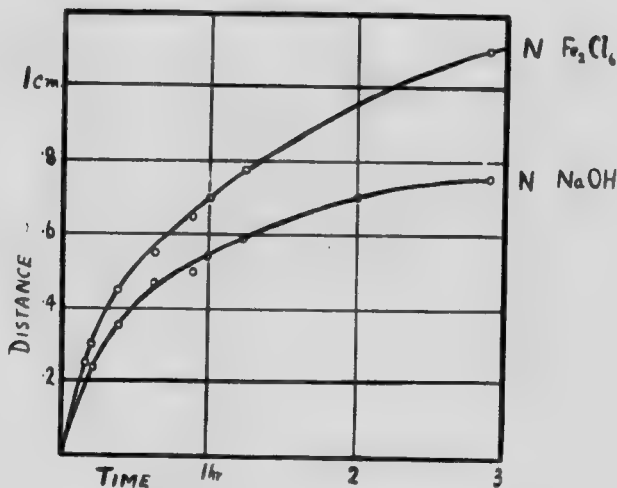


FIG. 10. Simple diffusion.

a precipitate is formed at some plane  $P$  at a distance  $d$  from the original silver diffusing front.

Then the concentrations of silver and chromate ions at  $P$  are  $V_a \cdot a$  and  $V_c \cdot c$  respectively. But the product of these two is

the precipitation value, so that  $\frac{V_a \cdot V_c \cdot a \cdot c}{d(D-d)}$  has a value which is susceptible of measurement, because  $A_0 \cdot C_0 = k \cdot X_0$ . (1)

Assuming that the distance  $D$  remains about the same for two or three consecutive bands, the condition for the formation of a precipitate is from (1)

$$\frac{V_a \cdot V_c \cdot a \cdot c}{d(D-d)} = k \cdot X \quad (2)$$

or, since  $V_a$  and  $V_c$  are constants for given concentrations and for a given temperature, the relation between the initial con-

centrations  $a$ , and  $c$ , and the distances between successive bands is of the form

$$d(D - d) = K.ac \quad \text{where } K \text{ is a constant.} \quad (3)$$

It seems legitimate to assume that  $D$  varies very slowly over the region occupied by a few consecutive bands. In these circumstances the variation of  $d$  with the product  $ac$  is exhibited graphically in fig. 6, the curve being a parabola having a maximum ordinate at  $d = D/2$ , when  $ac = \frac{1}{4} \frac{D}{K}$ .

It will be seen from this curve that as the concentration product  $a.c$  decreases, the distance between successive bands will diminish or increase according as  $d < \text{or } 1/2D$ . If the concentration product happens to take the value  $\frac{1}{4} \frac{D}{K}$  the bands will be equally spaced; otherwise they will be spaced at diminishing or increasing distances according as the rate of variation of  $a.c$  with  $d$  is positive or negative.

For most cases of outward diffusion of a strong solution against a weak solution  $d > 1/2D$  so that the usual result is that the bands are formed at successively increasing distances apart. An illustration of this is seen in the inner part of fig. 1. The outer part of the same figure illustrates equal spacing of the bands, which is only rarely obtained. An example of the third case, where the bands become successively closer, is discussed below. (See page 24.)

In some of the experiments described above measurements of distances of diffusion were made over an extended period, the results being plotted in the form of curves, with times as abscissae and distances as ordinates. These curves bring out clearly the way in which diffusion is prevented by approach of the molecular concentrations of the two reacting solutions toward the same point. They also show that in those cases where the diffusion proceeds rapidly at first there is a remarkably sudden drop in the rate of diffusion, and that this drop coincides with an almost uniform distance of diffusion. Some of these curves are reproduced in figs. 7 and 12. A comparison with figure 12 appears to indicate that the flat portions of the upper curves in figure 7 are due to a change in the viscosity of the gelatine.

A comparison of the curves for silver and lead solutions against the same concentrations of chromate solution shows that the lead diffuses the more slowly. This is in agreement with the higher rate of diffusion of the silver solution in pure gelatine.

From this a consideration of the possibility that the speed of

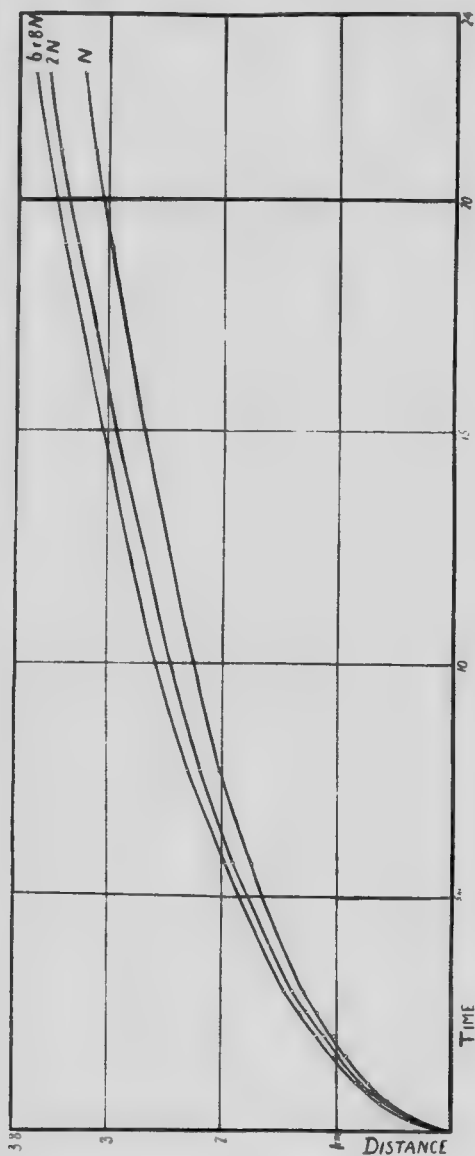


FIG. 11. Simple diffusion of silver nitrate of different strengths.

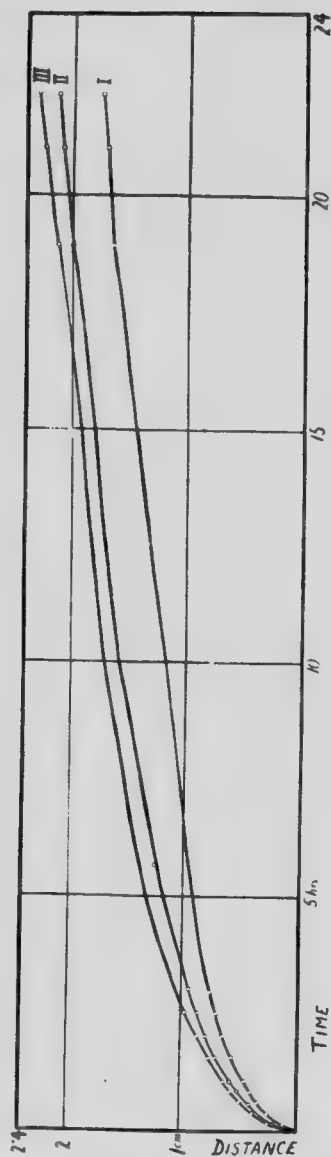


FIG. 12. Reaction  $4N \text{ AgNO}_3 / \frac{N}{200} \text{ K}_2\text{CrO}_4$  in gelatin of different strengths.

|      |                                 |         |                    |
|------|---------------------------------|---------|--------------------|
| I.   | 10 grs. gelatine in 53.5 cc. of |         |                    |
|      |                                 |         | gelatine solution. |
| II.  | do                              | 171 cc. | do                 |
| III. | do                              | 371 cc. | do                 |

the lead nitrate solution in gelatine may be less than that of the potassium chromate solution led to a measurement of the rates of diffusion of several solutions, in pure gelatine. Well-washed gelatine was placed on glass plates, allowed to set, and drops of different reagents of different strengths were placed upon them. The reagents diffused outwards. In some cases, e. g. silver nitrate, lead nitrate, ferric chloride, and sodium hydroxide, the diffusing solution had a clearly visible outline in the gelatine, which is susceptible of measurement. The measurements were made as before, by means of a millimeter scale, estimating to tenths of a millimeter, taking care to eliminate parallax. The diameter of the drop was taken and the diameter of the circle of diffusion (in the case of the precipitates above, to the outer limits of the precipitates). Subtracting the diameter of the drop from the total diameters of diffusion, and dividing by two the radius of diffusion is obtained. It is the rate of elongation of this radius which has been measured and plotted, and which is called the radius of diffusion here. The chromate solutions did not give a diffusing front which was clearly visible and susceptible of easy measurement. The yellow color due to the chromat-ions became gradually fainter away from the drop, coming to an indistinct and diffuse margin. Therefore, in the curves given in fig. 9 those for the chromate solutions are dotted, since they are not as reliable as the other curves.

The curves (see figs. 9, 10, 11) show that a strong solution of any reagent diffuses at a greater rate than a weaker solution of the same. They show that silver nitrate diffuses more rapidly than potassium chromate solutions of the same molecular concentrations. (The crossing of the silver and chromate curves cannot be regarded as established, for the reason stated above. Also the apparent straight lines of the chromate curves cannot be considered final determinations. The sudden stoppage appears to be correct, though this may be due to invisibility of the chromat-ion below a certain dilution.) It is certain that the lead nitrate solutions diffuse more slowly than the potassium chromate solutions of equal molecular strengths.

It was considered that this pair of reagents, the lead in outward, the chromate in inward diffusion, offered a good chance of testing the theory that with such a couple bands of precipitate might be formed which would become closer together outwards, instead of farther apart. Several different strengths of these reagents were tried against each other, the precipitates formed being apparently continuous to the naked eye. In the case of normal lead nitrate against N/200 potassium chromate an apparently continuous precipitate was formed. The hand lens showed no banding, but under the microscope the desired

result was observed. Toward the outer part of the precipitate a very fine banding was seen and the bands were closer together *outwards*. An attempt to reproduce this was not successful, owing to different hygroscopic character of the atmosphere, but a recent paper by Bradford (10) describes an experiment in which the diffusion of N/5 lead nitrate against N/10 potassium chromate, in a agar gel, gave rise to bands of precipitate which became *more closely spaced in the later deposited layers*. The first eight bands were 1.15<sup>mm</sup> apart, the ninth one being .9<sup>mm</sup> from the eighth. No chromate was left between the bands.

The same strengths of lead nitrate and potassium chromate used by Bradford were tried in gelatine. Three gelatine layers were placed in a test-tube, the lower one being a N/10 solution of potassium chromate, the middle layer being clear gelatine, and the upper one a N/5 solution of lead nitrate. Another test-tube was prepared with the same solutions reversed, the lower one being lead nitrate and the upper one potassium chromate. In both cases the chromate solution diffused the more rapidly so that the first formed precipitate was nearer to the starting point of the lead solution than to that of the chromate solution, while in both cases the later formed precipitate was on the side remote from the lead solution. With the chromate solution above the precipitate was a continuous mass, but when the lead solution was above the precipitate was formed in bands, which became closer and closer together, passing into a continuous mass. These experiments were repeated with the same results. This illustrates a controlling effect of gravity, which does not come into play when the diffusion takes place horizontally, as in the glass plate experiments.

#### *Miscellaneous Diffusions.*

In comparing the rates of diffusion of ferric chloride and sodium hydroxide the observation was made that ferric chloride possesses in a marked degree the property of inducing coagulation in gelatine, a property possessed by silver and lead nitrate solutions in a much smaller degree. This coagulant property of ferric chloride is well known. In comparing the rates of diffusion of the two reagents it was found, contrary to expectation, that the sodium hydroxide diffuses much more slowly than ferric chloride. (See fig. 10.) But the diffusion of the sodium hydroxide is not a simple case of diffusion. A reaction takes place with the gelatine, and this is at once apparent in the unexpected nature of the curve.

Diffusion of normal ferric chloride against N/100 and N/200 sodium hydroxide—(stronger solutions prevent the setting of the gelatine)—gave a colloidal precipitate of ferric hydroxide.

This is surrounded by a broad clear zone marked by a clearly visible circumferential line. The nature of this zone is unknown, at present.

A set of nine diffusions was carried out with 5N, 2N and N potassium iodide against N/20, N/40 and N/80 lead nitrate, and another set of nine with 2N, N, and N/2 lead nitrate against N/20, N/40 and N/80 potassium iodide. Probably owing to the state of the gelatine (not thoroughly free from acid) the precipitates were colloidal and not visibly banded except in the cases of 2N and N potassium iodide against N/20 lead nitrate, which showed fine rings to microscopical examination. They all showed that the diffusion proceeds more rapidly with greater difference of concentrations of the two reagents and all showed a broad indefinite band around the drop in which the precipitate was thinner, and a broad band on the outside of it in which the precipitate was thicker. This was especially marked in the cases where potassium iodide was the diffusing reagent (the one in the drop). It was found that several of these plates developed a banded structure immediately upon being immersed in a solution of sodium hydroxide, which was used to clean the plates after they had dried. Thus, although the precipitate is present in colloidal form it is arranged in layers or bands, though these are invisible until some such reaction as that described shows their presence.

#### *Effect of Different Gelatine Concentration.*

The reaction 4N silver nitrate against N/200 potassium chromate was carried out in gelatine of different strengths, obtained by dilution of the one stock. Rings were formed, and the rates of diffusion were measured. The plot of these results confirms the result of Hausmann (*loc. cit.*) that increase of the gelatine concentration retards the diffusion.

The curves are almost parallel and the rates differ so slightly that the curves only begin to diverge very slightly toward the right. The measurements recorded in these curves are only rough, but they suggest that more careful measurements may be able to detect a numerical relation between the concentration of the gelatine and the amount of retardation.

#### *Summary and Conclusions.*

After giving a historical account of the work of earlier writers, the results of certain experiments are given, the main points of which may be summarized as follows:

1. The rate of diffusion of a reagent of given strength is retarded by increasing that of the reagent in the gelatine. Also, the total distance to which diffusion takes place is de-



creased by a similar increase of strength of the reagent in the gelatine.

2. With too close approach of the concentrations of the two reagents, silver nitrate and potassium chromate, a continuous precipitate is formed, but under the microscope, the surface of this is seen to be finely banded. These fine bands follow the same rules as regards spacing as are found with the separated bands.

3. Separated bands are best produced by the diffusion of a strong silver solution against a weak chromate solution. (For other reagents, these conditions may not be universal.)

4. Similar results are obtained by diffusion of a strong chromate solution against a weak silver solution. But the particles formed are larger in this case.

5. Increase in distance between bands has been held to be due to progressive dilution of the reagents. Rate of diffusion is shown to be an important controlling factor, and that under certain conditions the bands may be equally spaced, or may be spaced at decreasing distances. These conditions are discussed.

6. The rates of diffusion of different reagents in pure gelatine are found to differ; thus potassium chromate diffuses more rapidly than a lead nitrate solution of the same molecular concentration, and a silver nitrate solution more rapidly than a potassium chromate solution. Also, a strong solution of any given reagent diffuses more rapidly than a weak solution.

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